

# Heavy-Mass Behavior of Ordered Perovskites $ACu_3Ru_4O_{12}$ ( $A = Na, Ca, La$ )

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We synthesized  $ACu_3Ru_4O_{12}$  ( $A = Na, Na_{0.5}Ca_{0.5}, Ca, Ca_{0.5}La_{0.5}, La$ ) and measured their DC magnetization, AC susceptibility, specific heat, and resistivity, in order to investigate the effects of the hetero-valent substitution. A broad peak in the DC magnetization around 200 K was observed *only* in  $CaCu_3Ru_4O_{12}$ , suggesting the Kondo effect due to localized  $Cu^{2+}$  ions. However, the electronic specific heat coefficients  $\gamma$  exhibit large values not only for  $CaCu_3Ru_4O_{12}$  but also for all the other samples. Moreover, the Wilson ratio and the Kadowaki-Woods ratio of our samples are all similar to the values of other heavy-fermion compounds. These results question the Kondo effect as the dominant origin of the mass enhancement, and rather indicate the importance of correlations among itinerant Ru electrons.

**KEYWORDS:** transition-metal oxide, ordered perovskite, ruthenium oxide, heavy fermion, electron correlation, Kondo effect

## 1. Introduction

A-site ordered perovskite oxides  $ACu_3B_4O_{12}$  (where  $A$  is alkaline-earth metals, rare-earth metals or some other elements, and  $B$  is transition metals) have recently been extensively studied, because rich varieties of electronic and magnetic properties are realized by various combinations of  $A$  and  $B$  ions.<sup>1)</sup> For example, insulating  $CaCu_3B_4O_{12}$  ( $B = Ti$ ,<sup>2-6)</sup>  $Ge$ ,<sup>7,8)</sup>  $Sn$ <sup>8)</sup>) exhibit antiferromagnetism for  $B = Ti$ <sup>6)</sup> and ferromagnetism for  $B = Ge$  and  $Sn$ . Such variation is crucially decided by the  $d$  electrons in the  $B$  ion shells, rather than the ionic radii of the non-magnetic  $B$  ions.<sup>8)</sup> Semiconducting  $CaCu_3B_4O_{12}$  ( $B = Mn$ ,<sup>9-11)</sup>  $Fe$ <sup>12,13)</sup>) exhibit giant magnetoresistance originating from their ferrimagnetic ordered states. Metallic  $CaCu_3B_4O_{12}$  ( $B = V$ ,<sup>14,15)</sup>  $Cr$ ,<sup>16,17)</sup>  $Co$ ,  $Ru$ <sup>18-26)</sup>) exhibit Pauli paramagnetic behavior. The crystal structure of  $ACu_3B_4O_{12}$  is depicted in Fig. 1. The  $A$  and  $Cu$  ions order in the  $A$ -site of the perovskite  $ABO_3$  in the ratio of one to three. The  $B$  and  $O$  ions form  $BO_6$  octahedra that share the oxygen atoms at the corner and the octahedra are in many cases severely tilted.

Among these  $A$ -site ordered perovskite oxides,  $ACu_3Ru_4O_{12}$ <sup>18)</sup> ( $A = Na, Ca, La$ ) has attracted much attention, because of its metallic conductivity with a heavy effective mass reported by Ramirez *et al.*<sup>20)</sup> and Kobayashi *et al.*<sup>21)</sup> These two groups disclosed the metal-insulator transition in  $ACu_3Ti_{4-x}Ru_xO_{12}$  ( $A = Na, Ca, La$ ). Ramirez *et al.*<sup>20)</sup> additionally compared the resistivity and the specific heat of the  $A$ -site substituted systems. In  $CaCu_3Ru_4O_{12}$ , Kobayashi *et al.*<sup>21)</sup> found magnetic behavior ascribable to the lattice Kondo effect between the localized  $Cu^{2+}$  ions with  $s = 1/2$  spins and the itinerant electrons originating from the  $Ru$   $4d$  orbitals. They further argued that the mass enhancement is attributable to the Kondo effect. In contrast, on the basis of the band structure calculation using exchange correlation functional, Xiang *et al.*<sup>25)</sup> recently

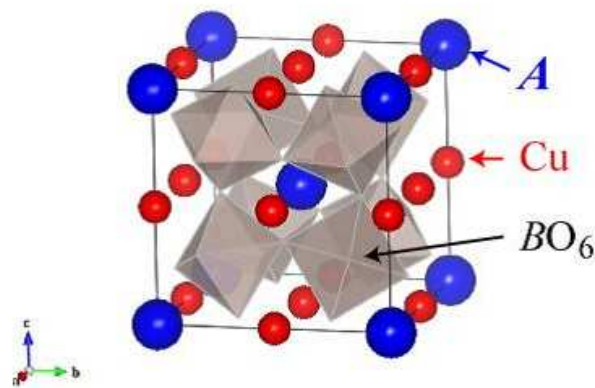


Fig. 1. (Color online) Crystal structure of  $ACu_3B_4O_{12}$ . Each of the octahedra is  $BO_6$ , in which the  $B$  ion is located at the center and the  $O$  ions occupy the corners. Each  $O$  ion is shared by two octahedra. The small red spheres represent  $Cu$  atoms and the large blue spheres represent  $A$  atoms. The figure is generated using the program "VESTA".<sup>27)</sup>

suggested that both the  $Ru$   $4d$  band itself and a mixed band where the  $Ru$   $4d$  band hybridizes with the nearly localized  $Cu$   $3d$  band might contribute to the heavy-mass behavior. Quite recently, Krimmel *et al.*<sup>26)</sup> reported the possibility of non-Fermi-liquid behavior below 2 K in  $CaCu_3Ru_4O_{12}$  based on the specific heat and the spin-lattice relaxation rate.

At present, it is not conclusive whether or not the Kondo effect is dominant or ever effective for the observed mass enhancement. Thus, it is useful to examine compounds in which the formal valence of  $Cu$  is shifted from  $2+$  in order to weaken the Kondo effect. This can be done by substituting  $Ca^{2+}$  ions in order not to introduce direct disorder at the  $Cu$  or  $Ru$  site. We compare the physical properties of  $CaCu_3Ru_4O_{12}$  with those of  $NaCu_3Ru_4O_{12}$  and  $LaCu_3Ru_4O_{12}$  to examine the

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Kondo scenario. (Note that the formal valence of Cu would be equal to  $2+$  for  $\text{Ca}^{2+}$  and deviate from  $2+$  as the valence of A-site varies from  $2+$ .) Kobayashi *et al.*<sup>21)</sup> controlled the heavy-mass behavior by substituting Mn for the Cu site or Ti for the Ru site, but these substitutions introduce much disorder at the Cu or Ru site, which are considered responsible for the electric conductivity. Because the Cu and Ru sites are directly involved in the Kondo mechanism, the A-site substitution without disorder at the Cu and Ru sites may be more useful to examine the origin of the mass enhancement of  $\text{CaCu}_3\text{Ru}_4\text{O}_{12}$ .

The main discussion in this paper is on the dominant origin of the mass enhancement of  $\text{ACu}_3\text{Ru}_4\text{O}_{12}$  ( $A = \text{Na}, \text{Ca}, \text{La}$ ), based on the measurements of the susceptibility, specific heat, and resistivity. The electronic specific heat coefficients  $\gamma$  of all our samples are relatively large compared with those of transition-metal oxides without strong correlations but comparable to the ruthenate superconductor  $\text{Sr}_2\text{RuO}_4$ <sup>28,29)</sup> with strong correlations. Moreover the effective mass of  $\text{LaCu}_3\text{Ru}_4\text{O}_{12}$  is even heavier than that of  $\text{CaCu}_3\text{Ru}_4\text{O}_{12}$ . This result indicates that the Kondo effect does not play a dominant role for the mass enhancement of  $\text{CaCu}_3\text{Ru}_4\text{O}_{12}$ . Otherwise,  $\gamma$  of  $\text{CaCu}_3\text{Ru}_4\text{O}_{12}$  would be the largest. For all our samples, the Wilson ratio and the Kadowaki-Woods ratio correspond well to other heavy-fermion compounds. These ratios provide additional evidence that the Kondo effect is not the dominant origin. Nevertheless, the susceptibility-maximum in  $\text{CaCu}_3\text{Ru}_4\text{O}_{12}$  implies the presence of the Kondo effect. We propose that the correlations among itinerant Ru electrons are dominant for the mass enhancement and the Kondo effect provides a minor contribution to the mass enhancement.

## 2. Experimental

Samples of  $\text{ACu}_3\text{Ru}_4\text{O}_{12}$  were synthesized with a conventional solid state reaction. Well ground stoichiometric mixtures of powders of  $\text{Na}_2\text{CO}_3$ ,  $\text{CaCO}_3$ ,  $\text{La}_2\text{O}_3$ ,  $\text{CuO}$ , and  $\text{RuO}_2$  were pressed into pellets, placed in alumina crucibles, and heated and kept at  $1000^\circ\text{C}$  for about 1 day. Only for  $\text{NaCu}_3\text{Ru}_4\text{O}_{12}$ , we used 5% less  $\text{RuO}_2$  since unreacted  $\text{RuO}_2$  was detected when we used a stoichiometric mixture. Then they were reground, pelletized, and heated, and kept at  $1000^\circ\text{C}$  for about 1 day. By repeating this procedure for 1–3 times, we obtained the polycrystalline samples of  $\text{Na}_{0.5}\text{Ca}_{0.5}\text{Cu}_3\text{Ru}_4\text{O}_{12}$ ,  $\text{CaCu}_3\text{Ru}_4\text{O}_{12}$ ,  $\text{Ca}_{0.5}\text{La}_{0.5}\text{Cu}_3\text{Ru}_4\text{O}_{12}$ , and  $\text{LaCu}_3\text{Ru}_4\text{O}_{12}$ . It is difficult to synthesize  $\text{NaCu}_3\text{Ru}_4\text{O}_{12}$  because of its lower melting point  $851^\circ\text{C}$ . We first heated the ground mixture at  $750^\circ\text{C}$ , and the reground mixture was pelletized and heated at  $900^\circ\text{C}$ . Then, the sample consisting of fine single crystals shown in Fig. 2 was obtained. To characterize these samples, we used powder X-ray diffractometry with the  $\text{CuK}\alpha_1$  radiation. As shown in Fig. 3, we confirm that the impurity peaks of  $\text{CuO}$  and  $\text{RuO}_2$  are estimated less than 4% from the X-ray diffraction patterns, indicating almost single-phase samples. The cubic lattice parameter  $a$  systematically increases from  $0.739\text{ nm}$  for  $A = \text{Na}$  to  $0.748\text{ nm}$  for  $A = \text{La}$  (See Table I).

The DC susceptibility was measured from  $1.8\text{ K}$  to  $350\text{ K}$

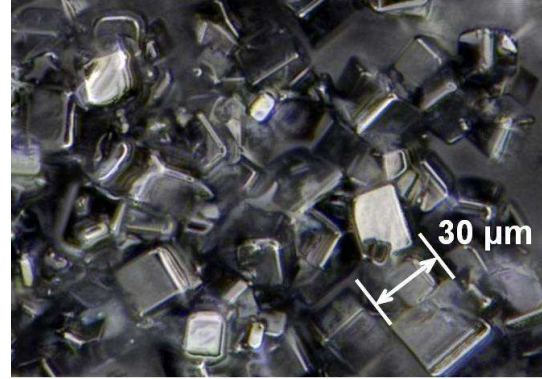


Fig. 2. (Color online) Optical microscope image of single crystals of  $\text{NaCu}_3\text{Ru}_4\text{O}_{12}$ . Obtained crystals are black and have a cubic shape with a side length of up to about  $50\text{ }\mu\text{m}$ .

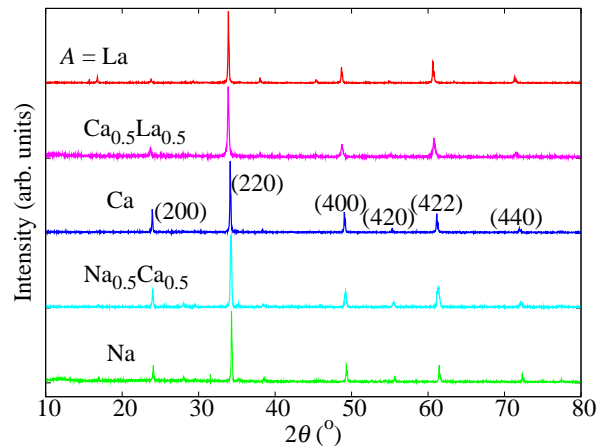


Fig. 3. (Color online) Powder X-ray diffraction patterns of  $\text{ACu}_3\text{Ru}_4\text{O}_{12}$  at room temperature, demonstrating nearly single-phase samples with the structure shown in Fig. 1.

with a commercial SQUID magnetometer (Quantum Design, model MPMS), and the specific heat from  $2\text{ K}$  to  $300\text{ K}$  with a commercial calorimeter (Quantum Design, model PPMS). The resistivity was measured from  $2\text{ K}$  to  $350\text{ K}$  using a standard four-probe method with DC or AC current. We measured the resistivity on at least three samples from each batch and confirmed their reproducibility. The AC susceptibility is measured by a mutual inductance method down to  $20\text{ mK}$  using a  $^3\text{He}$ - $^4\text{He}$  dilution refrigerator (Cryoconcept, model DR-JT-S-100-10).

## 3. Results

Figure 4(a) displays the measured DC susceptibility  $\chi = M/H$  at  $10\text{ kOe}$  from  $2\text{ K}$  to  $350\text{ K}$ . The susceptibility of  $\text{CaCu}_3\text{Ru}_4\text{O}_{12}$  has a distinct broad maximum at around  $200\text{ K}$ . In contrast, such a distinct peak is absent in the other samples. We note that the susceptibility of our samples contain smaller Curie tails at low temperatures than those reported by

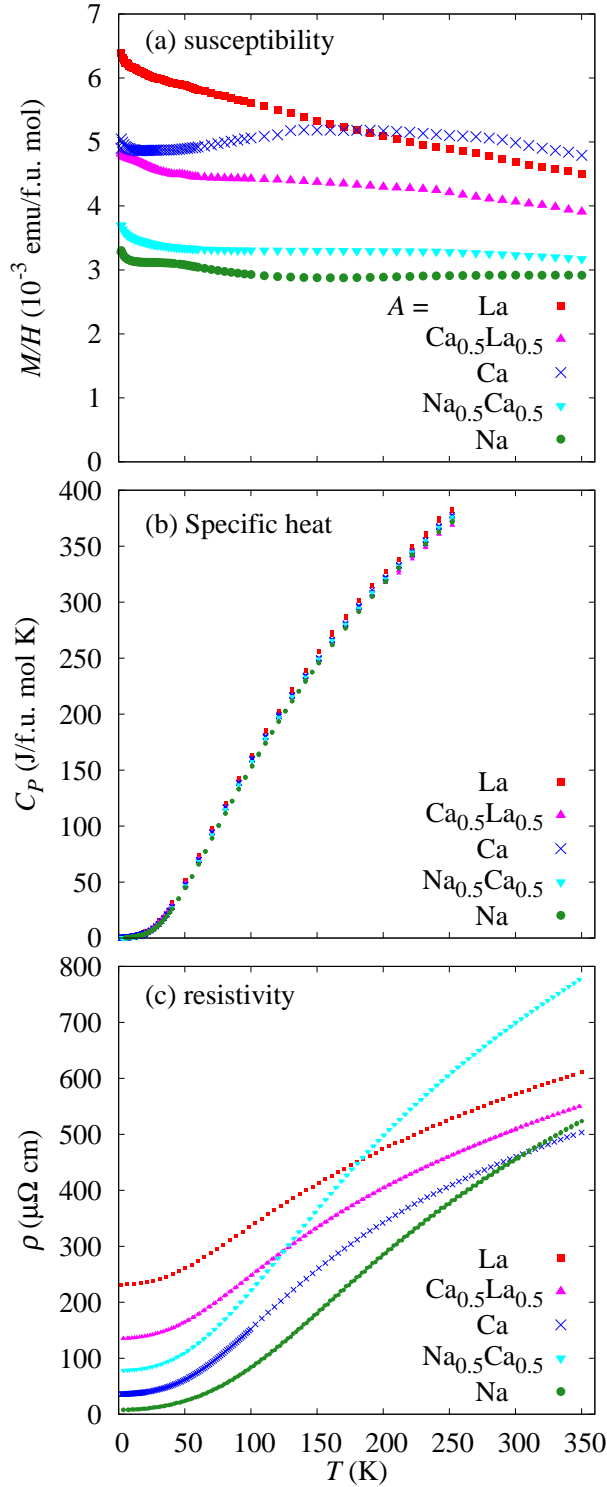


Fig. 4. (Color online) Temperature dependence of (a) the susceptibility  $\chi = M/H$  under 10 kOe, (b) the specific heat  $C_P$ , and (c) the resistivity  $\rho$  of  $\text{ACu}_3\text{Ru}_4\text{O}_{12}$ .

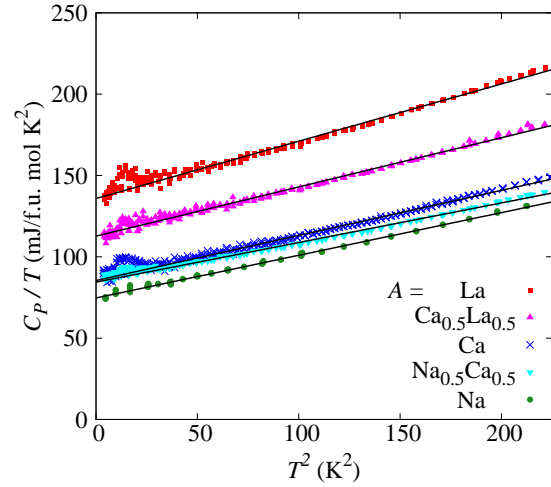


Fig. 5. (Color online) Variation of the specific heat of  $\text{ACu}_3\text{Ru}_4\text{O}_{12}$  divided by temperature,  $C_P/T$ , as a function of  $T^2$ . The lines are obtained by fitting the equation  $C_P/T = \gamma + \beta T^2$  to the data from 5 K to 15 K.

Labeau *et al.*<sup>18)</sup> and Krimmel *et al.*<sup>26)</sup> Among our samples of  $\text{CaCu}_3\text{Ru}_4\text{O}_{12}$ , there is a systematic tendency of an increase in the susceptibility at the broad peak at 200 K as the Curie tail becomes smaller. In search of possible superconductivity of these metallic compounds, we measured the AC susceptibility of all the samples down to 20 mK, but found no evidence for any magnetic transitions.

Figure 4(b) shows the specific heat  $C_P$ . There are no indications of magnetic transitions. The  $C_P$ - $T$  curves of all the samples are similar and  $C_P$  seem to approach around 400 J/f.u. mol K at 300 K (f.u.: formula unit). These values correspond to 80% of the value estimated from the Dulong-Petit law  $C_V = 3NR \approx 499$  J/f.u. mol K, where  $N = 20$  is the number of atoms per formula unit, and  $R$  is the gas constant.

$C_P/T$  as a function of  $T^2$  in a low temperature range is shown in Fig. 5. The solid lines represent the fitting  $C_P/T = \gamma + \beta T^2$  from 5 K to 15 K. We note that in this paper the values of  $\gamma$  are given per formula unit. For  $\text{CaCu}_3\text{Ru}_4\text{O}_{12}$ , for example,  $\gamma = 85$  mJ/f.u. mol  $\text{K}^2$  corresponds to  $\gamma = 28$  mJ/Cu mol  $\text{K}^2$ , consistent with the earlier reports.<sup>20,21,26)</sup> The values of  $\gamma$  of the other samples are also large and in particular  $\text{LaCu}_3\text{Ru}_4\text{O}_{12}$  has the largest  $\gamma$ . In fact, as the A-site ions vary from  $\text{Na}^+$  to  $\text{La}^{3+}$ ,  $\gamma$  exhibits a systematic increase. The Debye temperatures  $\Theta_D$  of all these samples are evaluated to be about 500 K using the relation  $\Theta_D = (12\pi^4 NR/5\beta)^{1/3}$ .

Fig. 4(c) represents the resistivity  $\rho$  of all the samples. In order to characterize the temperature dependence at low temperatures, we fit the relation  $\rho(T) = \rho_0 + A'T^\alpha$  to the data using  $\rho_0$ ,  $A'$ , and  $\alpha$  as the fitting parameters. The resulting exponents  $\alpha$  for all members lies within  $2.0 \pm 0.2$  below 25 K, demonstrating the  $T^2$  behavior. This quadratic temperature dependence is also evident in Fig. 6, where  $\rho - \rho_0$  is plotted against  $T^2$ . The coefficients  $A$  of the  $T^2$  term listed in Table I are eval-

Table I. Parameters characterizing the physical properties of  $\text{ACu}_3\text{Ru}_4\text{O}_{12}$ . The  $\chi_{10\text{K}}$  values are extracted from the raw data of  $M/H$ .  $\gamma$ ,  $\beta$ ,  $A$ , and  $\rho_0$  are obtained by fitting  $C_P/T = \gamma + \beta T^2$  from 5 K to 15 K and  $\rho = \rho_0 + AT^2$  up to 25 K. Using these parameters, we evaluate: Debye temperature  $\Theta_D$ , Wilson ratio  $R_W$ , Kadowaki-Woods ratio  $a_{\text{KW}} \equiv A/\gamma^2$ , volumetric electronic specific heat coefficient  $\gamma_v$ , Hussey's Kadowaki-Woods ratio  $a_{\text{KWH}} \equiv A/\gamma_v^2$  with  $b_0 = 1 \mu\Omega \text{ cm K}^2 \text{ cm}^6/\text{mJ}^2$ , and Jacko's Kadowaki-Woods ratio in three-dimensional systems  $a_{\text{KWJ}}$ .

A-site ions	lattice parameter $a$ (nm)	$\chi_{10\text{K}}$ ( $10^{-3}$ emu/f. u. mol)	$\gamma$ (mJ/f. u. mol $\text{K}^2$ )	$\beta$ (mJ/f. u. mol $\text{K}^4$ )	$A$ ( $\text{n}\Omega \text{ cm}/\text{K}^2$ )	$\rho_0$ ( $\mu\Omega \text{ cm}$ )
La	$0.7477 \pm 0.0001$	6.17	136	352	10.2	231
$\text{Ca}_{0.5}\text{La}_{0.5}$	$0.7460 \pm 0.0001$	4.72	113	303	10.8	135
Ca	$0.7421 \pm 0.0001$	4.72	85	277	8.5	36
$\text{Na}_{0.5}\text{Ca}_{0.5}$	$0.7407 \pm 0.0002$	3.56	84	243	10.2	78
Na	$0.7386 \pm 0.0001$	3.14	75	262	6.1	8

A-site ions	$\Theta_D$ (K)	$R_W$	$a_{\text{KW}}$ ( $(\mu\Omega \text{ cm}/\text{K}^2)/(\text{mJ}/\text{Ru mol K}^2)^2$ )	$\gamma_v$ ( $\text{mJ}/\text{cm}^3 \text{ K}^2$ )	$a_{\text{KWH}}$ ( $\mu\Omega \text{ cm K}^2 \text{ cm}^6/\text{mJ}^2$ )	$a_{\text{KWJ}}$
La	480	3.3	$0.9 \times 10^{-5}$	1.08	$0.009 b_0$	458
$\text{Ca}_{0.5}\text{La}_{0.5}$	505	3.1	$1.3 \times 10^{-5}$	0.90	$0.013 b_0$	662
Ca	519	4.0	$1.8 \times 10^{-5}$	0.69	$0.018 b_0$	845
$\text{Na}_{0.5}\text{Ca}_{0.5}$	543	3.1	$2.1 \times 10^{-5}$	0.69	$0.021 b_0$	963
Na	529	3.1	$1.7 \times 10^{-5}$	0.62	$0.016 b_0$	684

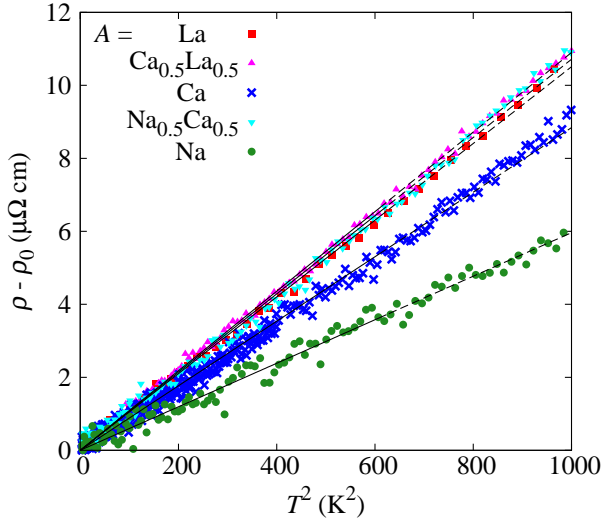


Fig. 6. (Color online) Temperature-dependent part of the resistivity  $\rho - \rho_0$  plotted against  $T^2$  for  $\text{ACu}_3\text{Ru}_4\text{O}_{12}$ .

uated by the fitting with  $\rho(T) = \rho_0 + AT^2$  below 25 K.

#### 4. Discussion

In this section we examine the origin of the mass enhancement in  $\text{ACu}_3\text{Ru}_4\text{O}_{12}$  from the relations among electronic specific heat coefficients  $\gamma$ , the susceptibility values  $\chi_{10\text{K}}$ , and the coefficients  $A$  of the  $T^2$  term in the resistivity.

We evaluate the Wilson ratio  $R_W \equiv \pi^2 k_B^2 \chi_0 / (3\mu_B^2 \gamma)$ , using  $\chi_0 = \chi_{10\text{K}}$  obtained at 10 K. Theoretically the value of  $R_W$  equals 1 for a free electron gas, whereas it approaches 2 in the strong correlation limit for local Fermi liquids. It may become greater than 2 if ferromagnetic fluctuations are present. The size of the deviation from unity is regarded as a measure of the strength of many-body electron correlations.  $R_W$  of the present compounds are all above 3 and comparable to that of

some other heavy-fermion compounds.

The relation between  $\gamma$  and  $A$  is described by the Kadowaki-Woods ratio<sup>30)</sup>  $a_{\text{KW}} \equiv A/\gamma^2$ , which is  $1 \times 10^{-5} (\mu\Omega \text{ cm}/\text{K}^2)/(\text{mJ}/\text{mol K}^2)^2$  for some typical heavy-fermion metals. If  $\gamma$  is expressed in terms of  $\text{mJ}/\text{Ru mol K}^2$ ,  $a_{\text{KW}}$  of  $\text{ACu}_3\text{Ru}_4\text{O}_{12}$  ( $A = \text{Na, Ca, La}$ ) are all around  $1 \times 10^{-5} (\mu\Omega \text{ cm}/\text{K}^2)/(\text{mJ}/\text{Ru mol K}^2)^2$ , consistent with such universality. In order to remove the ambiguity in the choice of the unit of  $\gamma$ , Hussey<sup>31)</sup> recently proposed the modified definition  $a_{\text{KWH}} \equiv A/\gamma_v^2$ . Here a molar quantity  $\gamma$  is rescaled to the volumetric quantity  $\gamma_v \equiv \gamma Z / (N_A a^3)$ , where  $Z$  is the number of formula units per unit cell,  $N_A$  is Avogadro's number, and  $a$  is a lattice parameter. The modified ratio for all  $\text{ACu}_3\text{Ru}_4\text{O}_{12}$  is evaluated as  $a_{\text{KWH}} \approx 0.01\text{--}0.02 b_0$ , where  $b_0 \equiv 1 \mu\Omega \text{ cm K}^2 \text{ cm}^6/\text{mJ}^2$ . We note that the rescaled values for all the present compounds happen to be very similar to that of a three-dimensional,  $d$ -electron heavy-fermion-like oxide  $\text{LiV}_2\text{O}_4$ <sup>32)</sup> ( $a_{\text{KWH}} \approx 0.02 b_0$ ).

Following Hussey's work, Jacko *et al.*<sup>33)</sup> very recently proposed an extended definition of the Kadowaki-Woods ratio applicable to a wide variety of heavy fermions, transition metals, transition-metal oxides, and organic charge transfer salts. They introduced the dimensionless ratio  $a_{\text{KWJ}} \equiv 4\pi\hbar k_B^2 e^2 f_d(n) (A/\gamma_v^2)$ , where the function  $f_d(n)$  is expressed in terms of the electron density  $n$  and spatial dimensionality  $d$  of a system. They further proposed the universality  $a_{\text{KWJ}} = 81$ . If we assume that  $\text{CaCu}_3\text{Ru}_4\text{O}_{12}$  contains 16 conduction electrons per formula unit of  $\text{Ru } 4d^4$ , the electron density is estimated to be  $n = 16Z/a^3$ , and we obtain  $a_{\text{KWJ}} \approx 880$  using  $f_3(n) = \sqrt[3]{3n^7/\pi^4\hbar^6}$  for a spherical Fermi surface. This evaluation is based on a crude single-band picture. Considering the change in the number of conduction electrons, the values of  $a_{\text{KWJ}}$  for the other  $\text{ACu}_3\text{Ru}_4\text{O}_{12}$  also lies within a factor of 2 (See Table I). Although these values are an order of magnitude larger than the universal value proposed by Jacko *et al.*, they are within the range of the values for other highly-correlated electron systems.



As shown in Table I,  $\gamma$ ,  $\chi_{10K}$ , and  $A$  exhibit almost systematic increases with varying the  $A$ -site ions from  $\text{Na}^+$  to  $\text{La}^{3+}$ . These parameters are closely related to the density of states  $D(\epsilon_F)$ :  $\gamma$  and  $\chi_{10K}$  are expected to be proportional to  $D(\epsilon_F)$  and  $A$  is expected to be proportional to  $D^2(\epsilon_F)$  for Fermi liquids.

Now we attempt to explain these systematic increases first from the standpoint of the rigid band model with the total density of states spectra obtained by the band calculation of  $\text{CaCu}_3\text{Ru}_4\text{O}_{12}$  using exchange correlation potential (shown in Fig. 3 in Ref. 25). A rigid band model relies on the approximation that the change in the valence of an ion induced by some site substitution results only in a shift of  $\epsilon_F$  without changing the band structure. For  $\text{CaCu}_3\text{Ru}_4\text{O}_{12}$ , when we substitute  $\text{Na}^+$  ( $\text{La}^{3+}$ ) for  $\text{Ca}^{2+}$ , that is, when the number of the conduction electrons decreases (increases),  $\epsilon_F$  would shift to lower (higher) energy in the calculated spectra. Assuming the rigid band model,  $D(\epsilon_F)$  would decrease (increase) since the calculated spectra has a positive slope around the Fermi energy  $\epsilon_F$ ;  $\gamma$ ,  $\chi_{10K}$ , and  $A$  would all decrease (increase). From a crude estimation using the calculated spectra,  $D(\epsilon_F)$  deviate  $\sim \pm 25\%$  by substituting  $\text{Na}^+$  or  $\text{La}^{3+}$  (13.4, 17.4, and 22.0 electrons/eV for  $A = \text{Na}$ ,  $\text{Ca}$ , and  $\text{La}$ , respectively). These  $A$ -site substitution results with the rigid band model are reasonably consistent with our observation and support that  $\gamma$  of  $\text{CaCu}_3\text{Ru}_4\text{O}_{12}$  should be mainly enhanced by the band itself. The present analysis implies that the changes in the lattice parameter plays a secondary role in the mass enhancement, consistent with the interpretation by Ramirez *et al.*<sup>20)</sup>

To date it has been proposed that the Kondo effect between the localized Cu  $3d$  and the itinerant Ru  $4d$  electrons may be the origin of the heavy effective mass since the behavior of the maximum around 200 K of the  $\chi$ - $T$  curve of  $\text{CaCu}_3\text{Ru}_4\text{O}_{12}$  is similar to that of the  $f$ -electron heavy fermion compound  $\text{CeSn}_3$ .<sup>34)</sup> We should stress here that indeed we observe the peak in  $\chi(T)$  ascribable to the Kondo effect only for  $\text{CaCu}_3\text{Ru}_4\text{O}_{12}$  (See Fig. 4(a)). However, if the Kondo effect is the dominant origin for the mass enhancement of  $\text{ACu}_3\text{Ru}_4\text{O}_{12}$ , a largest value of  $\gamma$  is expected for  $\text{CaCu}_3\text{Ru}_4\text{O}_{12}$ . In reality,  $\text{CaCu}_3\text{Ru}_4\text{O}_{12}$  is not the only one which has a large  $\gamma$  value. The other members, in which the formal valence of Cu ions is shifted from (localized)  $2+$ , also have large  $\gamma$  values. It is clear that the Kondo effect cannot be the dominant origin of the mass enhancement of  $\text{ACu}_3\text{Ru}_4\text{O}_{12}$ .

## 5. Conclusion

We investigated basic physical properties of  $\text{ACu}_3\text{Ru}_4\text{O}_{12}$  ( $A = \text{Na}$ ,  $\text{Na}_{0.5}\text{Ca}_{0.5}$ ,  $\text{Ca}$ ,  $\text{Ca}_{0.5}\text{La}_{0.5}$ ,  $\text{La}$ ) to low temperatures. Not only the electronic specific heat coefficients of  $\text{CaCu}_3\text{Ru}_4\text{O}_{12}$ , in which the formal valence of Cu ions is  $2+$  leading to localized Cu  $3d$  electrons, but also that of the other members of  $\text{ACu}_3\text{Ru}_4\text{O}_{12}$  are relatively large. This fact is inconsistent with the scenario that the Kondo effect plays a dominant role for the mass enhancement of  $\text{CaCu}_3\text{Ru}_4\text{O}_{12}$ .

Nevertheless, since we observed the maximum in  $\chi(T)$

only in  $\text{CaCu}_3\text{Ru}_4\text{O}_{12}$  around 200 K, which is similar to the maximum for  $f$ -electron heavy fermion compounds  $\text{CeSn}_3$ , the correlation between the localized Cu  $3d$  and the itinerant Ru  $4d$  electrons (Kondo effect) may in part contribute to the mass enhancement of  $\text{CaCu}_3\text{Ru}_4\text{O}_{12}$  to minor extent. The Kondo effect derived from the localized  $\text{Cu}^{2+}$  electrons cannot be totally neglected for  $\text{CaCu}_3\text{Ru}_4\text{O}_{12}$ .

The Wilson ratio and Kadowaki-Woods ratio of the present compounds exhibit values similar to those of other heavy-fermion compounds, suggesting the mass enhancement of  $\text{CaCu}_3\text{Ru}_4\text{O}_{12}$  originating mainly from the correlation among the Ru  $4d$  electrons. The electronic specific heat coefficient  $\gamma$ , the susceptibility value  $\chi_{10K}$ , and the  $\rho$ - $T^2$  coefficient  $A$  exhibit almost systematic increases with varying the valence of  $A$ -site ions from  $1+$  to  $3+$ . A simple rigid band model can account for our experimental results, supporting that the heavy mass arising from the Ru bands and the shape of the bands are important.

More systematic investigation is under progress to characterize the precise variations of  $\gamma$  for other combinations of the  $A$ -site. At the same time it is desirable to determine the valence states of Cu and Ru ions in  $\text{ACu}_3\text{Ru}_4\text{O}_{12}$  to clarify the roles of the localized and itinerant Cu electrons.

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